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Sensitivity of N_2O, $CFCl_3$, and CF_2Cl_2 Two-Dimensional Distributions to O_2 Absorption Cross Sections

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The distribution of the trace gases N_2O, $CFCl_3$, and CF_2Cl_2 is influenced by the O_2 absorption cross sections. There has been a recent indication in the literature that the O_2 cross sections used in past model studies may overestimate the true values. We have used a two-dimensional model to perform a sensitivity study on the effects of changes in the O_2 cross sections on N_2O, $CFCl_3$, and CF_2Cl_2. Decreases in the O_2 cross sections between 180 and 230 nm resulted in altitude-, latitude-, and season-dependent reductions in the computed species' concentrations. The altitude dependence of the reductions at mid-latitudes agrees qualitatively with similar one-dimensional model studies (Froidevaux and Yung, 1982; Brasseur et al., 1983). The vertical profiles of $CFCl_3$ are most affected and the vertical profiles of N_2O are least affected by the O_2 cross-section changes. The greatest changes in the trace gases occur above 20 km, at high latitudes, and in the winter. In general, the reduced O_2 cross sections led to better agreement between model calculations and experimental measurements for all three trace gases; however, there still remain some unexplained differences between observations and model predictions. This result implies that the reduced O_2 cross sections may be the better set. The accuracy of the lifetime calculations for the trace gases is not sufficient to recommend either set of O_2 cross sections. More precise measurements of O_2 absorption cross sections are thus required to determine the true values.

INTRODUCTION

A good test of the transport and ultraviolet radiation treatment for any model is provided by the three gases N_2O, $CFCl_3$ (F-11), and CF_2Cl_2 (F-12). These species all have their major sources at the ground and their major sinks in the stratosphere. If the profiles for these species are well represented by a model, then that model is doing a respectable job of representing both the long-term vertical transport and the radiation field. Because the wavelength region of the absorption cross sections for O_2 overlaps the wavelength region for absorption by N_2O, $CFCl_3$, and CF_2Cl_2, a change in the O_2 cross sections can result in a change in the profiles for these trace gases. We fix the transport scheme but change the UV radiation through adjustments in the O_2 absorption cross sections.

Frederick and Mentall [1982], using balloon measurements of solar flux, suggested that there should be a reduction in the commonly used O_2 cross sections between 200 and 210 nm. *Herman and Mentall* [1982] extended the wavelength region to between 200 and 225 nm over which the reduction in O_2 cross sections should be applied. One-dimensional models [e.g., *Froidevaux and Yung*, 1982; *Brasseur et al.*, 1983] have used the O_2 cross sections suggested by *Herman and Mentall* [1982]. They show significant decreases in trace gas concentrations when using the smaller O_2 cross sections.

One-dimensional models include transport of gases using vertical eddy diffusion coefficients in order to represent a global average of the vertical transport. We use a two-dimensional model (discussed by *Guthrie et al.* [1984]) which allows us to study changes in seasonal and latitudinal distributions that result from O_2 cross-section changes. A latitude-dependent ozone decrease has already been predicted by two-dimensional models for chlorofluoromethane (CFM) release [see *Borucki et al.*, 1980]; thus it is of interest to determine if a strong latitude-dependent change is detectable in the CFM profiles. The one-dimensional models pointed toward a trend of decreased trace gas concentrations in correlation with decreased O_2 cross sections. We change the O_2 cross sections between 180 and 230 nm within a range of experimentally allowed values. We then study the distribution of N_2O, F-11, and F-12, relate our model results to observations, and contrast our sensitivity runs.

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ABSORPTION CROSS SECTIONS BETWEEN 180 AND 230 NM

The absorption cross sections for F-11 and F-12 are from *World Meteorological Organization* [1982]. The absorption cross sections for N_2O are taken from *Selwyn et al.* [1977]. The largest sink for these three gases is photodissociation; however, there also is some loss due to reaction with $O(^1D)$. Reactions used in these tracer studies are given by *Guthrie et al.* [1984].

Several measurements of O_2 cross sections exist in the literature for wavelengths short of 230 nm. We do not discuss the experimental measurements that exist for O_2 but refer the reader to *Brasseur et al.* [1983], who discuss and compare a few of them. We used several different sets of O_2 cross sections in our sensitivity runs. We only compare the results from the two sets taken at the extremes of the range of O_2 cross sections. The first set of cross sections (used in case A) is a combination of *Allen and Frederick* [1982] below 200 nm and *Hasson and Nicholls* [1971] above 200 nm. This first set is close to the cross-section set used in most other active photochemical models. The second set of cross sections (used in case B) is a combination of the "corrected" Allen and Frederick cross sections (see below) below 200 nm and *Herman and Mentall* [1982] above 200 nm.

The "corrected" Allen and Frederick cross sections were found in the following manner: *Frederick and Mentall* [1982] suggested that the *Shardanand and Prasad Rao* [1977] cross sections for wavelengths between 200 and 210 nm should be multiplied by 0.9 to 1.0. Following this suggestion, we multiply the Shardanand and Prasad Rao cross sections at 200 nm by a factor of 0.9 and get a value of 9×10^{-23} cm^2. For wavelengths between 180 and 200 nm we correct the *Allen and Frederick* [1982] Schumann-Runge band cross sections (which contain continuum cross sections from *Hudson and Mahle*

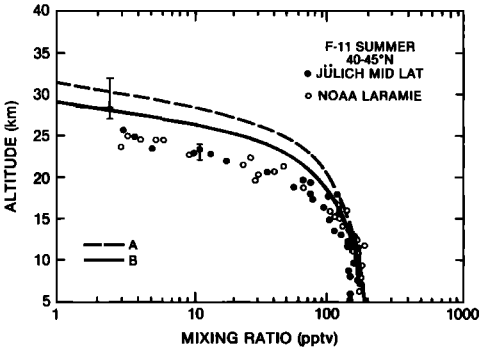

Fig. 1. Mid-latitude summer vertical profiles of F-11. Data points are taken from *World Meteorological Organization* [1982], which see for references. The dashed line (case A) uses the higher set of O_2 cross sections, and the solid line (case B) uses the lower set of O_2 cross sections.

[1972]) using the 200-nm value as a reference cross-section value. Multiplying the Hudson and Mahle cross sections by 0.7 ties them to 9×10^{-23} cm^2 at 200 nm. The *Allen and Frederick* [1982] Schumann-Runge band cross sections are thus "corrected" by subtracting a factor of 0.3 times the Hudson and Mahle cross sections.

Model Runs

We used the two-dimensional model described by *Guthrie et al.* [1984] for our studies. The only input change in each study was a change in the O_2 cross section. The O_3 was fixed at the Nimbus 7 observed distribution [*McPeters et al.*, 1984], updated monthly. This was done in all of the studies so that the O_3 would be consistent. F-11 and F-12 were input into the model at historical release rates [*Bauer*, 1979; *World Meteorological Organization*, 1982]. The N_2O mixing ratio was fixed at 300 ppb at the ground. For the base case the model was run from 1960 up to 1974 using the O_2 cross sections from case A. Since the model required a large amount of VAX 780 computer time (approximately 2 hours of computer time for 1 year of model time), we started each of the sensitivity runs from this 1974 base case stopping point and ran up through 1980.

Several cases were run with different O_2 cross sections. The runs were then compared in the year 1980. Because of the relatively small changes that resulted in the trace gas profiles when comparing the several cases we will only concern ourselves with the two extremes of the range of O_2 cross sections, represented by cases A and B. Among the several parameters which help reflect the differences in the runs are the species' profiles, two-dimensional photodissociation rate and density differences, total difference with respect to month of the year, and lifetime differences.

Comparison of Model Runs

Our results are very similar to those of *Froidevaux and Yung* [1982] and *Brasseur et al.* [1983]: a reduction in the O_2 cross section leads to generally better agreement between the model trace gas profiles and the experimental measurements. As an example of this we present the profiles of F-11 for the mid-latitude region in summer in Figure 1. The dashed line represents the case A run, and the solid line line represents the case B run. The amount of F-11 above 20 km is, however, overestimated in both of the runs. This implies that errors may exist in the F-11 photoabsorption cross sections or that another loss of F-11 is not accounted for in our model.

We see a larger difference between cases A and B at the higher altitudes and the higher latitudes. The three gases F-11, F-12, and N_2O are illustrated in Figure 2. The percent difference P_n plotted in this figure was calculated by

$$P_n(\theta, z) = \frac{n_{Ai}(\theta, z) - n_{Bi}(\theta, z)}{n_{Ai}(\theta, z)} * 100 \quad (1)$$

where $n_{Ai}(\theta, z)$ and $n_{Bi}(\theta, z)$ are the densities for the ith species at latitude θ and altitude z in cases A and B, respectively. The plot is for day 33.5, which corresponds to midwinter in the northern hemisphere. A seasonal difference can also be observed. For most latitudes and altitudes the winter season shows the largest percent difference.

In general, both transport and photochemistry are important in determining the structure of a trace gas two-dimensional distribution. Since the transport is fixed in this model study, the change in the photochemistry (resulting from a change in the O_2 absorption cross sections) is most important in altering the trace gas two-dimensional distribution; however, the influence of the transport is not insignificant.

The J coefficients are larger at the higher altitudes; thus smaller percent differences between cases A and B are reflected in larger changes in the resultant species' concentrations. Higher latitudes have larger solar zenith angles and, therefore, larger optical depths. Changes in the O_2 absorption cross sections, which contribute to the optical depth, are reflected in larger changes in the J coefficient for the trace gas. This optical depth dependence also produces seasonal differences. Wintertime has associated with it larger solar zenith angles than the summertime and thus also larger changes in the J coefficient.

The largest hemispheric difference (in total number of molecules) between cases A and B is computed to be in the northern hemisphere near midwinter for F-11 and F-12. Since the F-11 and F-12 release rates are biased toward the northern hemisphere, the total amounts of F-11 and F-12 are biased toward the northern hemisphere, and the total difference observed between cases A and B is greater in the northern hemisphere. N_2O with a constant mixing ratio boundary condition at all latitudes shows no hemispheric bias, but the difference in N_2O content does show a peak in midwinter. The percent difference contours of N_2O appear flatter but do tend to mimic the mixing ratio contours reasonably well, especially in the middle to high latitudes. Both F-11 and F-12 exhibit a similar behavior. The shape of the trace species concentration is preserved in the two cases, A and B; thus the basics of this shape will be transferred to the percent difference contour plots. The transport, therefore, has an influence and the largest differences occur at midwinter and not at winter solstice.

The larger percent changes in the J coefficients are observed at the higher altitudes for a constant pressure level, but the total number of molecules is less per 10° latitude band at the higher latitudes. We find that this results in an optimal place for the largest difference (in total number of molecules per 10° latitude band) to be in the mid-latitudes between 25° and 45° for all three gases. The optimal place is at a larger latitude for F-11 and at a smaller latitude for N_2O with F-12 between the two extremes. Because of its smaller photodissociation rate, N_2O can be transported to higher altitudes where the difference in J coefficients between the various latitudes for a given pressure level is smaller.

Comparison of Lifetimes

Because of the effects that F-11 and F-12 have on ozone [e.g., *Molina and Rowland*, 1974], it is important to know the

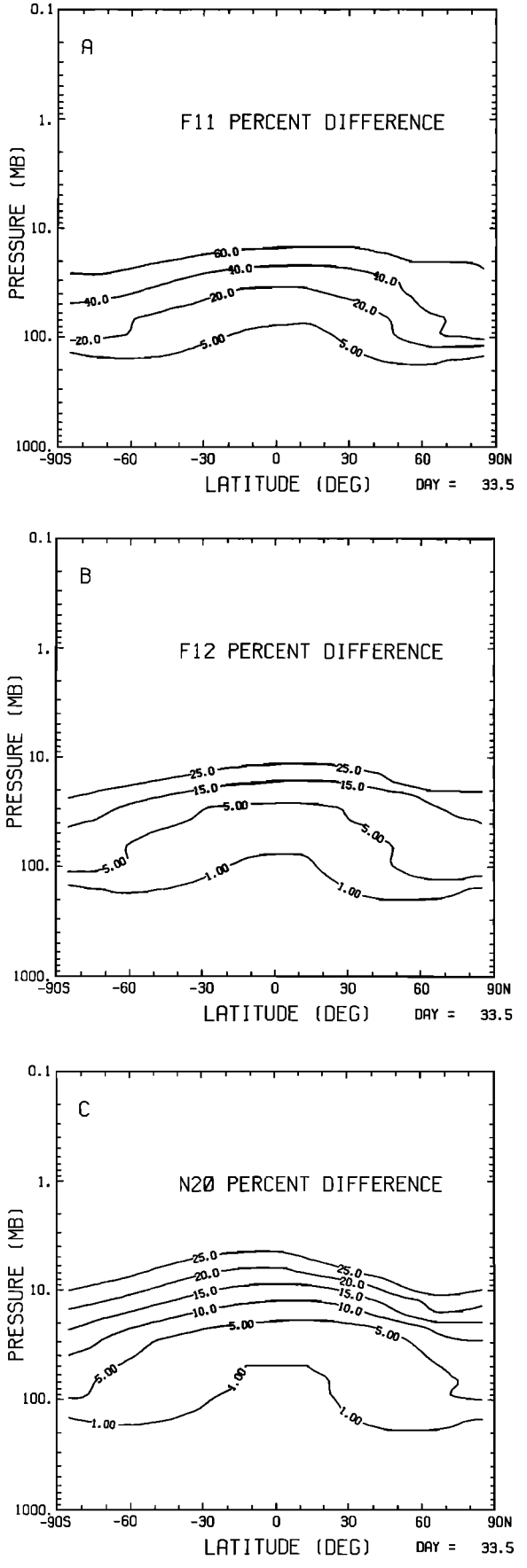

Fig. 2. Percent differences in number densities between cases A and B as functions of pressure and latitude for (*a*) F-11, (*b*) F-12, and (*c*) N_2O. Equation (1) was used to calculate the differences.

lifetimes of these species. A smaller lifetime for the CFM's leads to a smaller effect on ozone [*Cunnold et al.*, 1978]. The atmospheric lifetime experiment (ALE) is an important undertaking to determine the lifetimes of chlorine-containing trace gases. The major results from ALE are presented as lifetimes [*Cunnold et al.*, 1978, 1983*a*, *b*; *Prinn et al.*, 1983]. In this section we compare the lifetimes calculated for the three species in the two cases with other lifetimes measured or computed by others. The lifetimes T_{Ln} for species n were calculated using

$$T_{Ln} = \frac{\int_{1\text{yr}}\int_{-90}^{90} c(t,\theta)\sin\theta\, d\theta\, dt}{\int_{1\text{yr}}\int_{-90}^{90}\int_{0}^{\text{top}} L_n S_n \sin\theta\, dz\, d\theta\, dt} \quad (2)$$

where L_n is the photochemical loss rate for species n at altitude z (s^{-1}), S_n is the density of species n at altitude z (cm^{-3}), and $c(t, \theta)$ is the column content (cm^{-2}) of species n at time t and latitude θ. The information from the year 1980 was used to calculate the lifetimes for each trace gas in the respective model runs. Table 1 presents the lifetimes from our two cases with several others that have been published in the literature.

The lifetime defined by (2) is an e-folding loss time for the present global burden if all sources were turned off. Two recent papers using two-dimensional models similar to ours have published lifetimes. If we compare our range of values to these [*Ko and Sze*, 1982; *Owens et al.*, 1982], we find that our range includes their values. The lifetime of F-11 calculated by *Brice et al.* [1982] using a two-dimensional model of the troposphere along with observations is 75 years with a two-sigma range from 65 to 90 years. Their result depends on a parameterization of the loss rate rather than calculated photolysis but does suggest that stratospheric photolysis is the only significant loss for F-11.

Cunnold et al. [1983*a*] also calculate the lifetime of F-11

TABLE 1. Comparison of Lifetimes (in Years) for the Trace Gases N_2O, F-11, and F-12

Reference	N_2O	F-11	F-12
Case A	196	67	154
Case B	159	47	118
Cunnold et al. [1983*a*]			
Trend technique		83^{+73}_{-27}	
Global inventory technique		70^{+89}_{-25}	
Cunnold et al. [1983*b*]			
Trend technique			>81
Global inventory technique			69^{+36}_{-18}
Brice et al. [1982]		75	
Ko and Sze [1982]	159	65	135
Owens et al. [1982]			
One dimensional		75	140
Two dimensional		60	120
World Meteorological Organization [1982]	100		
National Academy of Sciences [1979]		50	90
Levy et al. [1979]	150		
Hinds [1979]		81	182
United Kingdom Department of the Environment [1979]			
One dimensional, AERE		50	77
Two dimensional, Meteorology Office		50	118
Two dimensional, Oxford		78	133
Rasmussen and Pierotti [1978]	11–30		
Schmeltekopf et al. [1977]	100		
Sze and Wu [1976]	10–100		
Rowland and Molina [1975]		>20	>20
Schutz et al. [1970]	70		

using a two-dimensional model of the troposphere along with observations. *Cunnold et al.* [1983*b*] extend this calculation to F-12. Again the major loss for both gases is assumed to occur in the stratosphere. The annual average ground level mixing ratios are presented for F-11 and F-12 for both the northern and southern hemispheres by *Prinn et al.* [1983]. The ratios of the northern to southern hemisphere values are 1.09 (F-11) and 1.08 (F-12), whereas we compute the ratios to be 1.13 (F-11) and 1.12 (F-12). In our two-dimensional model calculation, however, we find that both F-11 and F-12 are fairly well mixed by 200 or 300 mbar [see *Guthrie et al.*, 1984]. Since the main losses for F-11 and F-12 are in the stratosphere, the differences between our model-calculated lifetimes and those from the ALE should not be affected by the northern to southern hemisphere ratio differences. We calculate the F-12 lifetime to be larger than the F-11 lifetime by greater than a factor of 2. This seems reasonable when comparing the F-11 and F-12 measurements. The F-12 profiles fall off with altitude at a slower rate than do those of F-11, indicating a longer lifetime for F-12 assuming only a ground source for F-11 and F-12. The results from *Cunnold et al.* [1983*a*, *b*], however, seem to indicate that the F-11 and F-12 lifetimes are in the same range, contrary to our results.

CONCLUSIONS

Lower O_2 absorption cross sections lead to larger photodissociation rates for the trace gases F-11, F-12, and N_2O. These then lead to lower values in concentration at all altitudes and latitudes. The sensitivity of the concentrations to uncertainties in these cross sections is greater at the higher altitudes, higher latitudes, and in the wintertime. The F-11 concentration values are changed the most by the O_2 cross-section changes, with the decrease in O_2 cross sections leading to smaller F-11 concentration values which agree better with measurements. The N_2O and F-12 concentration values are not changed as much as those of F-11 but in general give slightly better agreement with measurements if the O_2 cross sections are reduced. These results imply that the smaller O_2 absorption cross sections are the better set. The smaller O_2 cross sections lead to a smaller lifetime for CFM's in the atmosphere.

In the model studies of this paper we fix the O_3; however, another two-dimensional model study [*Crutzen and Schmailzl*, 1983] and other one-dimensional model studies [*Froidevaux and Yung*, 1982; *Brasseur et al.*, 1983] allowed O_3 to vary. These other studies found that the smaller O_2 cross sections lead to O_3 concentrations which are in worse agreement with measurements in the upper stratosphere than the O_3 concentrations computed using the larger O_2 cross sections. Because of these results and since uncertainties exist in the trace gas absorption cross sections as well as the transport scheme used in any two-dimensional model, neither set of O_2 absorption cross sections can be ruled as incorrect. We agree with the conclusions of Froidevaux and Yung and of Brasseur et al. that additional laboratory measurements of the O_2 cross sections as well as additional measurements of the solar flux in the middle stratosphere are required to determine the correct O_2 cross sections.

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